

PULSED SPUTTER DEPOSITED $\text{HfO}_x/\text{M}/\text{HfO}_2$ (M-Hf, Al) MULTILAYER ABSORBERS FOR SOLAR SELECTIVE APPLICATIONS

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ABSTRACT

Spectrally selective $\text{HfO}_x/\text{M}/\text{HfO}_2$ (M-Hf, Al) multilayer absorber coatings were deposited on copper substrates using a pulsed direct current unbalanced magnetron sputtering system. The compositions and thicknesses of the individual component layers were optimized to achieve high solar absorptance ($\alpha = 0.916\text{--}0.925$) and low thermal emittance ($\epsilon = 0.05\text{--}0.07$). The X-ray diffraction data showed that the $\text{HfO}_x/\text{Hf}/\text{HfO}_2$ coating consists of tetragonal and monoclinic phases of HfO_2 . The bonding structure of the HfO_2 layers was confirmed using X-ray photoelectron spectroscopy. In order to study the thermal stability of the $\text{HfO}_x/\text{M}/\text{HfO}_2$ (M-Hf, Al) coatings, they were subjected to heat treatment in air at different temperatures and durations. The $\text{HfO}_x/\text{Hf}/\text{HfO}_2$ coating deposited on Cu substrates exhibited high solar selectivity (α/ϵ) of 0.912/0.06 even after heat-treatment in air up to 400°C for 2 h. Whereas, $\text{HfO}_x/\text{Al}/\text{HfO}_2$ coating was thermally stable in air up to 350°C for 2 h. The structural stability of the absorber coatings heat-treated in air (up to 400°C) was confirmed by micro-Raman spectroscopy measurements.

Keywords: multilayer absorber, hafnium oxide, pulsed sputtering, micro-raman spectroscopy, thermal stability

1. INTRODUCTION

Transition metal oxide coatings such as Cr_2O_3 , MoO_3 , WO_x , etc. have been used for solar selective applications due to their excellent optical properties and good thermal stability [1]. Among these, hafnium oxide (HfO_2) coatings are technologically important because of their good mechanical, chemical and thermal stability as well as relatively high dielectric constant and high refractive index (n) [2]. The wide band gap (5.5 eV) of HfO_2 gives it transparency

V. Rajendran, B. Hillbrands, K. Thyagarajah and K.E. Geckeler (eds.)

Nanostructured Materials for Electronics, Energy and Environmental Applications, 319–324 (2010).

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over a wide spectral range, extending from the ultraviolet to the mid-infrared (IR) [3]. Due to its large band gap and high refractive index, HfO_2 is an interesting candidate for optical applications. HfO_2 is used as an optical coating for astronomically charged coupled devices, antireflective multilayer coating for night vision devices [4], high reflectivity mirrors and for IR optical devices [5].

The optical properties of single layer hafnium oxide thin films have been studied extensively [6-9]. To the best of our knowledge, HfO_2 based multilayer absorber coatings for high temperature solar thermal applications have not been developed and studied so far. In the present work, we have prepared an $\text{HfO}_x/\text{M}/\text{HfO}_2$ (M- Hf, Al) multilayer absorber coating with improved optical properties for high temperature solar selective applications. Asymmetric bipolar-pulsed DC generator was used to develop the $\text{HfO}_x/\text{M}/\text{HfO}_2$ multilayer absorber coatings on copper substrates. The structural, chemical and optical properties of these coatings have been studied using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), micro-Raman spectroscopy and solar spectrum reflectometer and emissometer.

2. EXPERIMENTAL DETAILS

$\text{HfO}_x/\text{M}/\text{HfO}_2$ (M- Hf, Al) coatings were prepared on Cu substrates (dimension: 35 mm \times 35 mm \times 2 mm) using a pulsed DC unbalanced magnetron sputtering system. Before putting the substrates into the vacuum chamber, they were metallographically polished and chemically cleaned. The vacuum chamber was pumped down to a base pressure of 5.0×10^{-4} Pa. High purity Hf (99.95%) target (diameter = 0.075 m) was used for the deposition of the coatings. An asymmetric bipolar-pulsed generator (frequency = 100 kHz, pulse width = 2976 ns, positive pulse bias = +37 V) was used to sputter the Hf target. The HfO_2 layer was prepared from the reactive sputtering of Hf target in Ar + O_2 plasma at a pressure of 1.0×10^{-1} Pa. For the deposition of the bottom HfO_x layer, the power density was 9 W/cm^2 and the oxygen flow rate was 6 sccm. The Hf metal layer was deposited from the non-reactive sputtering of the metal target in Ar plasma at a pressure of 1.0×10^{-1} Pa. Sputtering was carried out at a power density of 2.24 W/cm^2 for the Hf and Al metal layers. For the top HfO_2 layer, the power density was 9 W/cm^2 and the oxygen flow rate was 8 sccm. All the coatings were deposited at a substrate temperature of approximately 40-50°C.

In order to test the thermal stability, the $\text{HfO}_x/\text{M}/\text{HfO}_2$ (M- Hf, Al) coatings deposited on copper substrates were heated in air in a resistive tubular furnace at temperatures (T_A) in the range of 200-425°C for 2 h. Changes in the chemical composition of the solar selective coatings as a result of heating were measured using micro-Raman spectroscopy. A DIOR-JOBIN-YVON-SPEX integrated Raman spectrometer (Model Labram) was used for the present experiments.

3. RESULTS AND DISCUSSIONS

3.1 X-ray Diffraction

The XRD pattern of a typical $\text{HfO}_x/\text{Hf}/\text{HfO}_2$ (approximately 125 nm thick) coating deposited on Si substrate showed low intensity peaks centered at $2\theta = 38.32^\circ$ and 44.60° , which

correspond to (102) plane of $t\text{-HfO}_2$ and (211) plane of $m\text{-HfO}_2$, respectively. No peaks pertaining to crystalline Hf were observed in the XRD data. These results clearly indicate that the hafnium oxide present in the multilayer absorber coating exhibited a mixture of monoclinic and tetragonal phases. The bonding structure of the HfO_x and HfO_2 layers were confirmed by X-ray photoelectron spectroscopy data (Figures not shown here).

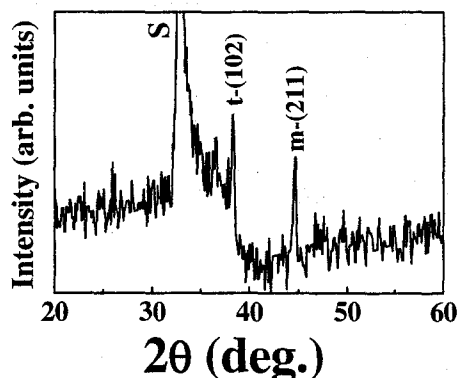


Fig. 1: Typical X-ray Diffraction Pattern of $\text{HfO}_x/\text{Hf}/\text{HfO}_2$ Multilayer Absorber Coating

3.2 Thermal Stability

The optimized $\text{HfO}_x/\text{M}/\text{HfO}_2$ (M- Hf, Al) coating deposited on Cu substrate exhibited a high absorptance of the order of 0.916-0.925 and a low emittance of 0.05-0.07 at 82°C. In order to study the thermal stability of the $\text{HfO}_x/\text{M}/\text{HfO}_2$ (M-Hf, Al) multilayer absorbers, the coatings were heat-treated in air at different temperatures for 2 h. The absorptance and the emittance values of the heat-treated multilayer absorbers are listed in Tables 1 and 2. It is clear from the Table 1 that for $\text{HfO}_x/\text{Hf}/\text{HfO}_2$ coatings, the absorptance and the emittance values did not change significantly even after heat-treatment at 400°C for 2 h. Whereas, $\text{HfO}_x/\text{Al}/\text{HfO}_2$ coatings were thermally stable in air up to 350°C. At $T_A = 400^\circ\text{C}$, the absorptance value for $\text{HfO}_x/\text{Al}/\text{HfO}_2$ coatings decreased ($\Delta\alpha = -0.100$) drastically and there was no change in the emittance value (see Table 2). This is because at temperatures greater than 350°C, copper from the substrate starts diffusing into the coating and its subsequent oxide formation results in optical degradation in the visible range and decrease of solar absorptance [10].

3.3 Micro-Raman Spectroscopy

The changes in the chemical composition of $\text{HfO}_x/\text{Hf}/\text{HfO}_2$ and $\text{HfO}_x/\text{Al}/\text{HfO}_2$ coatings at higher operating temperatures were studied using micro-Raman spectroscopy. The composite Raman spectra of the as-deposited and multilayer absorbers deposited on Cu substrates heat-treated up to 425°C are shown in Fig. 2. The as-deposited $\text{HfO}_x/\text{Hf}/\text{HfO}_2$ coating (Fig. 2a) shows six Raman bands centered at 118, 274, 325, 404, 549 and 653 cm^{-1} . The bands centered at 118, 274, 325 and 549 cm^{-1} are of A_g symmetry and the other bands centered at 404 and 653

cm^{-1} are attributed to B_g symmetry of $m\text{-HfO}_2$ [11]. At 400°C (Fig. 2b), the bands are broadened considerably indicating the change in the composition/microstructure of the multilayer coatings.

Table 1: Effect of 2 Hours Annealing (in air) on the Absorptance and Emittance Values of $\text{HfO}_x/\text{Hf}/\text{HfO}_2$ Coatings Deposited on Copper Substrates

Annealing Temperature ($^\circ\text{C}$)	α			ϵ		
	As-deposited	Annealed	$\Delta\alpha$	As-deposited	Annealed	$\Delta\epsilon$
200	0.917	0.917	0.000	0.07	0.07	0.00
300	0.925	0.925	0.000	0.06	0.06	0.00
400	0.923	0.912	-0.011	0.06	0.06	0.00
425	0.925	0.650	-0.275	0.05	0.04	-0.01

Table 2: Effect of 2 Hours Annealing (in air) on the Absorptance and Emittance Values of $\text{HfO}_x/\text{Al}/\text{HfO}_2$ Coatings Deposited on Copper Substrates

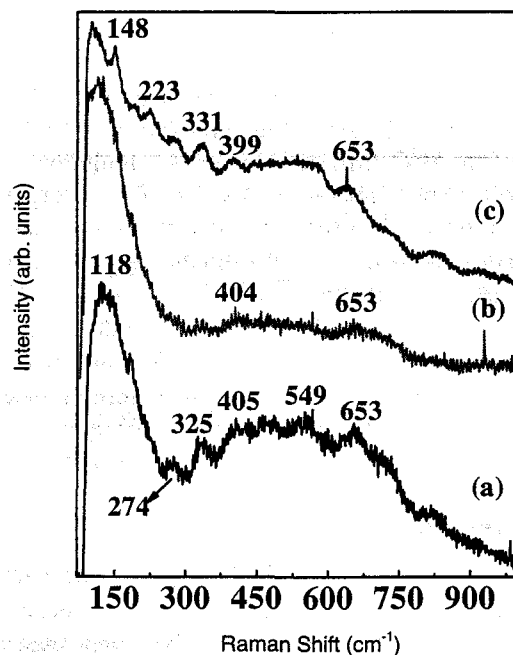


Fig. 2: Raman Spectra of: (a) As-deposited $\text{HfO}_x/\text{Hf}/\text{HfO}_2$ Coating on Cu Substrate and Coatings Heat-Treated in Air at (b) 400°C and (c) 425°C for 2 h

Annealing Temperature ($^{\circ}\text{C}$)	α			ϵ		
	As-deposited	Annealed	$\Delta\alpha$	As-deposited	Annealed	$\Delta\epsilon$
200	0.918	0.922	+0.004	0.07	0.06	-0.01
300	0.916	0.925	+0.009	0.07	0.06	-0.01
350	0.918	0.926	+0.008	0.07	0.06	-0.01
400	0.925	0.825	-0.100	0.06	0.06	0.00

Whereas, at 425°C (Fig. 2c), two new bands centered at 148 and 223 cm^{-1} were observed and also the shape of the Raman spectra was changed significantly. Figure 3 shows the composite Raman spectra of $\text{HfO}_x/\text{Al}/\text{HfO}_2$ multilayer absorbers heat-treated up to 400°C in air. The shape of Raman spectra did not change significantly even after heating the sample up to a temperature of 350°C , indicating the stable composition/microstructure of the multilayer coatings.

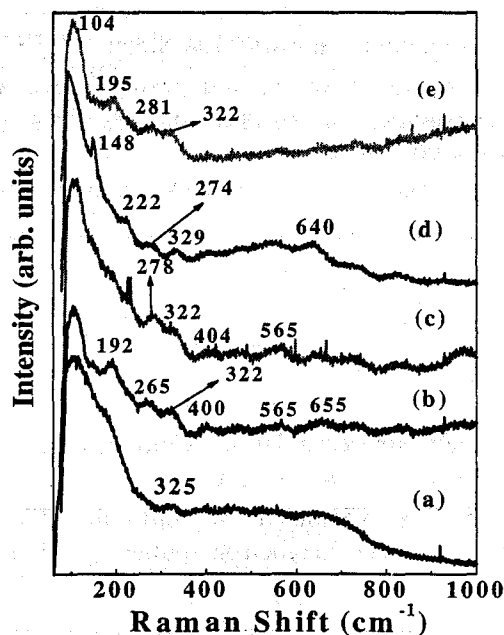


Fig. 3: Raman Spectra of: (a) As-deposited $\text{HfO}_x/\text{Al}/\text{HfO}_2$ Coating on Cu Substrate and Coatings Heat-treated in Air at (b) 300°C , (c) 350°C , (d) 375°C and (e) 400°C for 2 h

4. CONCLUSIONS

Asymmetric bipolar-pulsed DC generators were used to deposit $\text{HfO}_x/\text{M}/\text{HfO}_2$ (M-Hf, Al) solar selective coatings with high absorptance (0.916-0.925) and low emittance (0.05-0.07).

Heat-treatment of the $\text{HfO}_x/\text{Hf}/\text{HfO}_2$ coatings in air for 2 h showed that the coatings were stable up to 400°C with a solar selectivity of 0.912/0.06. Whereas, $\text{HfO}_x/\text{Al}/\text{HfO}_2$ coating was thermally stable in air up to 350°C for 2 h. The Raman data confirmed the microstructural stability of the coatings heat-treated in air at 400°C for 2 h.

ACKNOWLEDGEMENTS

The authors thank the Director, NAL (CSIR) for giving permission to publish these results.

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